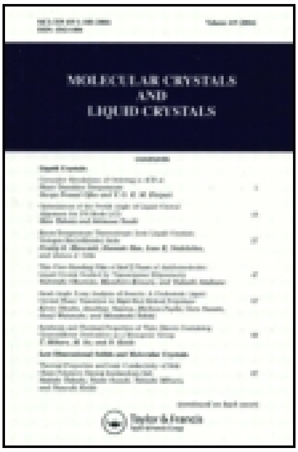

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Amide Bond Formation between Carboxylated Multi-Walled Carbon Nanotubes and Glass Surface by Using Carbodiimide Condensing Agent and Triazole Derivatives

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Amide bond formation between carboxylated multi-walled carbon nanotubes (MWCNT-COOHs) and aminated glass surface has been studied to make transparent conductive device. Examining the condensation reaction between MWCNT-COOHs and glass surface under various conditions, it has been found that MWCNT-COOHs are immobilized on the surface by reaction using a carbodiimide and a triazole. The MWCNT layers formed are not easily detached; the interaction between MWCNTs and glass surface is quite strong, implying formation of chemical bonding. Immobilization of MWCNTs on the surface is confirmed also by scanning electron microscopy. Electric conductivity of MWCNT-coated glass has been preliminarily measured.

Keywords Amide bond; carbodiimide; glass; multi-walled carbon nanotube; triazole

Introduction

Carbon nanotubes (CNTs) have recently received a lot of attention in fields such as material science, chemistry and medical technology. From the medical viewpoint, CNTs are considered promising for use as a cage or carrier for magnetic resonance imaging (MRI) reagent and other medical materials, including drugs in drug delivery systems (DDS), scaffolds for tissue engineering, bacteria trapping materials and so on [1–6]. In the MRI application, CNTs are particularly expected to act as a carrier of toxic substances with various body fluids and the subsequent damage may be avoided by using a CNT carrier. In the DDS applications, CNTs are expected to expand the kinds of drugs available for treatments; for example, this technique will be useful for direct injection of hydrophobic drugs into the blood-stream.

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CNTs are also expected to be a conductive material for novel electronic device production. Many attempts to make materials containing CNTs have been reported: chemical vapor deposition of CNTs on metal or glass surface [7–9], mixing of CNTs and a suitable binder for CNT-containing paste [10], vacuum filtration of a CNTs-dispersed solution [11], dropping of dispersion containing carboxylated CNTs onto glassy carbon and fabrication of CNT thin film [12], dropping of dispersion containing CNTs onto planar substrate and simple drying [13], coating of polystyrene dishes, collagen, titanium, and silicon rubber [14–17], and so on. However, these examples are mainly based on a physical (van der Waals) interaction. The binding force of a physical adsorption is weaker than that of chemical bonding. Therefore, relatively high external forces will easily remove CNTs from the substances. To avid this weakness, formation of chemical bonding is desirable.

In this study, we examined a condensation reaction using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) as a condensing agent to form covalent bond (amide bond) between poly-carboxylated multi-walled CNTs (MWCNT-COOHs) and aminated glass surface. This carbodiimide is known to be a effective reagent for amide bond formation through condensation reaction between amino and carboxyl groups [18]. In addition, two triazole derivatives, 1-hydroxybenzotriazole (HOBt) and 1-hydroxyazabenzotriazole (HOAt), were employed to enhance the reaction rate of condensation [19,20]. The MWCNT-coated glasses obtained were characterized by scanning electron microscopy, visible absorption spectroscopy and electric resistance measurement.

Experimental

Synthesis of MWCNT-COOHs

Chemicals employed for the synthetic procedure were multi-walled carbon nanotubes (MWCNTs), *o*-dichlorobenzene, succinic anhydride and hydrogen peroxide. MWCNTs were supplied by NanoLab (USA) while all other chemicals were supplied by Wako Chemicals (Japan). The chemicals other than MWCNTs were used without further purification. MWCNTs were heated at 500°C and washed with conc. hydrochloric acid to purify them in advance. MWCNTs (100 mg) were dried after the purification and dispersed in 100 cm^3 of *o*-dichlorobenzene with sonication. Succinic acid peroxide (10 g) prepared from succinic anhydride and hydrogen peroxide was then added into the solution and the mixtures were stirred at 80°C for 24 hours. Synthetic procedure of the peroxide has been reported by Peng et al. [21]. MWCNT-COOHs obtained were then vacuum-filtered, washed with tetrahydrofuran and ethanol, and dried at 70°C in the air.

Condensation between MWCNT-COOHs and Aminated Glass Surface

MWCNT-COOHs (20 mg) synthesized as described above were dispersed into 20 cm^3 of dried benzene with sonication. EDC hydrochloride and triazole derivatives, HOBt and HOAt, were supplied by Aldrich (USA) and Tokyo Kasei (Japan), respectively. EDC hydrochloride (3 mg) and one of the triazole derivatives (3 mg) were added into the solution. Aminated glass used was Matsunami S9441 MAS-coated glass (Matsunami Glass Ind. Ltd., Japan); this glass possesses amino groups on its surface. The glass plate was cut into small pieces of 30 mm × 13 mm rectangle. The glass piece was dipped into the solution and stirred at room temperature for 24 hours. After the reaction, the glass was washed with tetrahydrofuran with sonication and dried in the air.

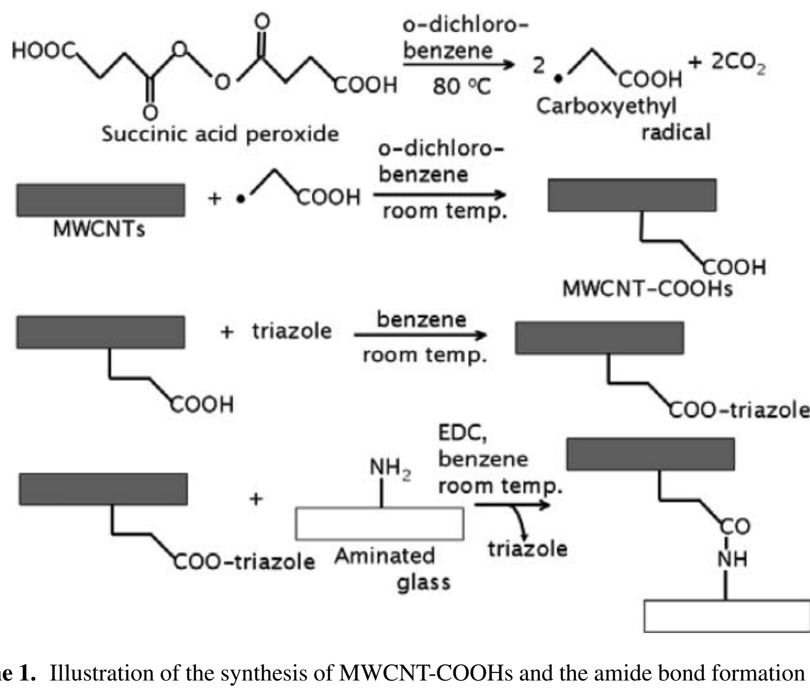
Characterization of MWCNT-Coated Glass

The binding strength between MWCNTs and glass surface was qualitatively checked by means of vigorous scratching with papers, scotch-tape test and sonication; we checked whether MWCNTs were detached from the surfaces by these treatments. The morphology of the MWCNTs on the glass surface was observed with a scanning electron microscope (SEM, JSM-6510LA, JEOL, Japan). Transparency of the glass substrates was measured with an ultraviolet-visible spectrophotometer (UV-120A, Shimadzu, Japan). The range of wavelength for the transparency measurement was 400–800 nm. Electric resistance of the glass pieces was measured with a setup constructed of an ammeter and a voltmeter. Electric circuit of the setup will be described below.

Results and Discussion

Fabrication of MWCNT-Coated Glass

Entire reaction of the synthesis of MWCNT-COOHs and the amide bond formation between MWCNT-COOHs and aminated glass surface is shown in Scheme 1. Synthetic procedure of MWCNT-COOHs is similar to the procedure reported previously [22–25]. In this study, EDC, HOBt and HOAt are employed as condensation agents. EDC is a well-known condensation agent in the field of peptide chemistry. HOBt and HOAt are known to enhance the rate of the condensation reaction. This effect is due to the formation of HOBt ester from corresponding carboxylic acid followed by the condensation reaction between the ester and amine.



Scheme 1. Illustration of the synthesis of MWCNT-COOHs and the amide bond formation between MWCNT-COOHs and aminated glass surface.

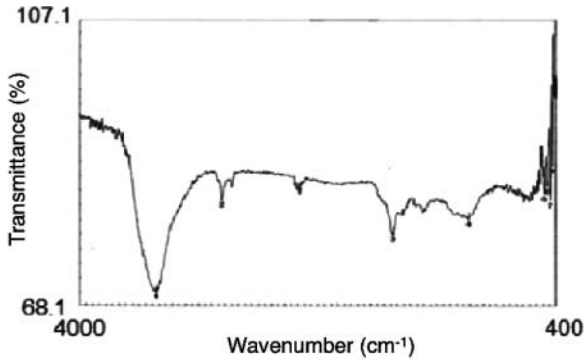


Figure 1. FT-IR spectrum of MWCNT-COOHs.

Introduction of carboxyl groups into MWCNTs was confirmed by means of acid-base titration and Fourier-transform infrared absorption (FT-IR) measurement (FT/IR-350, JASCO, Japan). Figure 1 shows the FT-IR spectrum of MWCNT-COOHs. On the basis of these measurements, carboxyl groups are successfully introduced into MWCNTs and

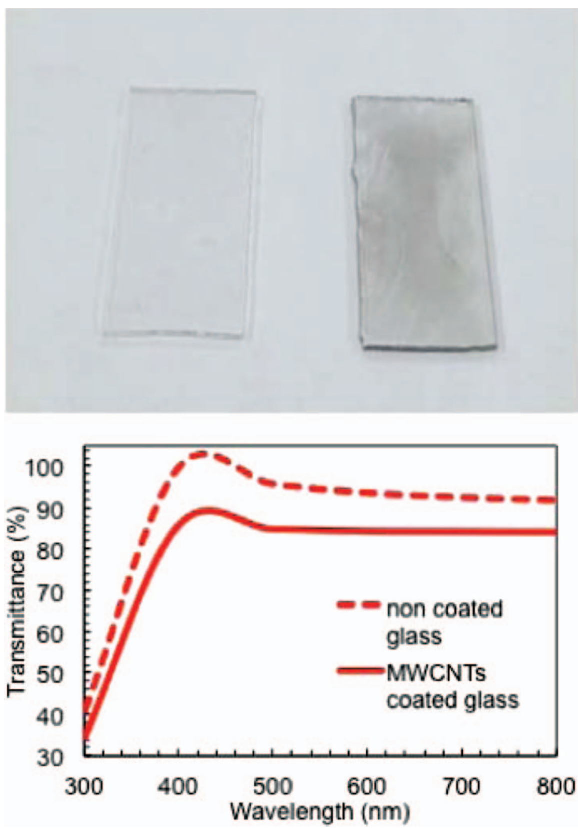


Figure 2. Photograph of pristine (left) and MWCNT-coated (right) glasses. Transmittance spectra of pristine and MWCNT-coated glasses are also shown.

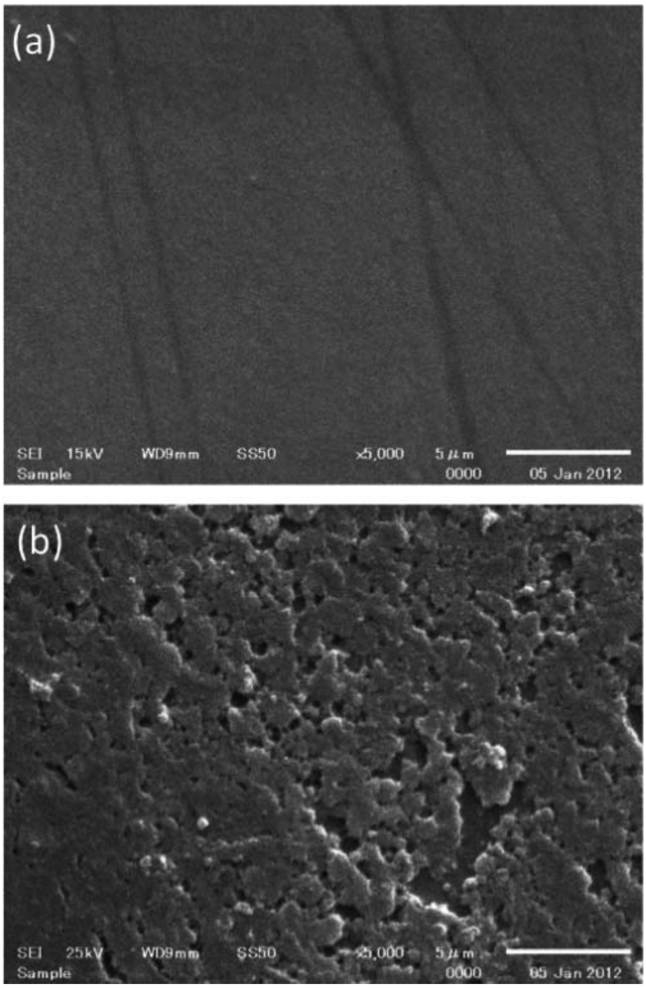


Figure 3. SEM images of pristine (a) and MWCNT-coated (b) glasses.

MWCNT-COOHs are formed. In the FT-IR spectrum of MWCNT-COOHs obtained, the characteristic absorption bands are appeared around 3300, 2900, 1700 and 1100 cm^{-1}. These bands are obviously assigned to O—H, C—H, C=O and C—O stretching modes of carboxyethyl groups, respectively.

Comparing the reaction rates of the condensation between MWCNT-COOHs and glass surface using HOBt and HOAt, a distinct difference in reaction rate was not confirmed at the moment. In general, HOAt is considered to be more improved agent, but the reaction behavior observed using one of the triazole derivatives is apparently similar to that observed using another one; finding the difference between HOBt and HOAt will be a further subject for future study.

Photograph of pristine and MWCNT-coated glasses is shown in Fig. 2. A glass before the condensation reaction is transparent, while after the reaction it changes to pale black. This indicates that MWCNTs are successfully attached on the glass surface. The layer of MWCNTs fabricated on the glass surface is not easily detached from the surface even by quite strong forces; the MWCNTs layer remains after vigorous scratching, adhesion and peeling of a scotch-tape piece and sonication. This indicates that the interaction between MWCNTs and a glass surface is quite strong, implying formation of chemical bonding.

Characterization of MWCNT-Coated Glass

SEM image of an MWCNT-coated glass is shown in Fig. 3. For comparison, SEM image of a pristine glass is also shown. No MWCNTs are found on the glass surface before the condensation. On the other hand, after the reaction layer of the remaining MWCNTs exist on the surface even after sonication.

Absorption spectra of the glasses were measured in the 300–800 nm region of wavelength. Transmittance spectrum of an MWCNT-coated glass is shown in Fig. 2 together with photograph of the glasses. The transmittance of visible light of MWCNT-coated glass was 84.2–85.8%. This is comparable to the value obtained for pristine glass (91.7–99.7%). The present result suggests that the MWCNT-coated glass obtained in this work will be used as a transparent MWCNT-containing material. As described below, this MWCNT-coated glass shows electric conductivity. Therefore, this material will be a possible candidate of conductive material for various purposes such as a transparent electric-stimulating scaffold for cell culturing and a self-heating sheet glass for defrosting.

Electric conductivity of the glasses was also preliminarily observed. Electric circuit for resistance measurement is illustrated in Fig. 4. Direct current is supplied by a constant-current DC source to the sample glass and resistance of the sample is obtained according to Ohm's law. The electric resistances measured for pristine and MWCNT-coated glasses are listed in Table 1. In the Table 1 the value obtained for MWCNT-coated glass prepared using EDC and HOBt is listed as the value for MWCNT-coated glass (the result of the glass prepared using EDC + HOAt is omitted). As easily expected, the resistance of pristine glass is quite high, indicating that the glass is an insulator. The resistance of the MWCNT-coated glass is somewhat lower than that of pristine glass; the difference in the resistance

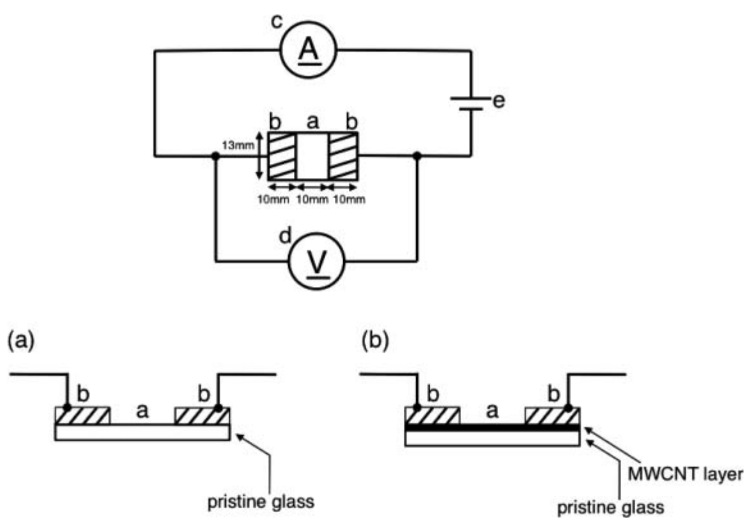


Figure 4. Setup for the electric resistance measurement: (a) sample (pristine or MWCNT-coated glass); (b) aluminum electrodes; (c) ammeter; (d) voltmeter; (e) constant-current DC supply. The structures of the samples are also shown: (a) pristine glass; (b) MWCNT-glass.

Table 1. Electric resistances measured for the glass substrates

Substrate	Resistance measured/MΩ
Pristine glass	9.89 ± 0.01
MWCNT-coated glass	9.83 ± 0.09

between the glasses is about 0.06 MΩ. Therefore, electric conductivity is provided to glass by attachment of MWCNTs on the surface. However, change in the electric resistance observed is only slight at the moment, and further improvement of procedure for high-density immobilization of MWCNTs should be necessary for practical application.

Conclusion

In this work we succeeded in immobilizing MWCNTs on aminated glass surface using EDC and a triazole derivative. MWCNTs and aminated glass surface bind to each other quite strongly and the MWCNTs are not detached easily; this result strongly supports the formation of amide bonds between MWCNTs and the surface. Preliminary electric resistance measurement shows that the addition of MWCNTs gives a glass surface electric conductivity. Remaining subjects for further study are direct confirmation of chemical bonding, establishment of reaction condition for higher-density immobilization of MWCNTs on glass surface, and improvement of electric conductivity.

Acknowledgments

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